Dielectric Normal Mode Process in Dilute Solutions of Poly(2,6-dichloro-1,4-phenylene oxide)

Keiichiro Adachi* and Tadao Kotaka

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

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ABSTRACT: Dielectric relaxation due to the fluctuation of the end-to-end distance of polymer chains, termed the normal mode process, has been studied for dilute solutions of poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO) in chlorobenzene. The frequency dependence of the dielectric loss factor at 300 K exhibits a maximum around 1 MHz, and the frequency f_m of the maximum loss decreases with increasing molecular weight. The molecular weight dependence of f_m is in accord with that calculated in terms of the Rouse–Zimm theory in the range $M < 2 \times 10^4$, but f_m is higher than the theoretical relaxation frequency in the range $M > 2 \times 10^4$. The Mark–Houwink–Sakurada relation for the intrinsic viscosity also changes at $M = 2 \times 10^4$. From these facts it is deduced that PDCPO with low molecular weight consists of linear chains but that PDCPO of higher molecular weight consists of branched chains. The relaxation frequency for the branched PDCPO was estimated on the basis of the Zimm–Kilb theory and compared with f_m. The width of the loss peak for the branched PDCPO was ascribed to the distribution of the chain length of the branches.

Introduction

Flexible polymer molecules in which the dipoles of the repeat units are uniaxially aligned in the direction parallel to the chain backbone have dielectric properties distinctly different from those of other polymers. The resultant polarization vector of such a polymer molecular coincides always with the end-to-end vector and hence the fluctuation of the end-to-end distance, the "nomal mode process", can be observed by means of the dielectric method.[1,2] The polarization of such a polymer in dilute solution was described theoretically by Zimm[3] and Stockmayer and Baur[4] in terms of the "bead–spring model" proposed by Rouse[5] and Bueche,[6] while the dielectric behavior of such a polymer in concentrated solution may be explained by the "tube theory" developed by de Gennes[7] and Doi and Edwards.[8]

Experimental studies of the normal mode process are, however, relatively rare.[9-13] Stockmayer et al. reported the dielectric relaxations of linear and branched poly(propylene oxides)[9,10] in the bulk state and those of poly(ϵ-caprolactone)[11] in solution. They found that the dielectric relaxation time for the normal mode process increases with molecular weight but that that for the segmental mode is independent of molecular weight. North and Phillips reported a normal mode process in poly(p-substituted phenylacetylene).[12]

In this paper, we report a study of the normal mode process in dilute solutions of poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO) in chlorobenzene. From the molecular structure of the repeat unit illustrated in Figure 1, PDCPO can be regarded as a polymer having only a uniaxially parallel component of the dipole moment, provided that the molecule does not contain chemical irregularities such as head-to-head linkages and branches.

Several methods are available for preparing PDCPO. Among these, two methods are known to give relatively high molecular weight PDCPO. One is that proposed by Blanchard et al.,[14] who prepared PDCPO by decomposition of a copper complex of 2,4,6-trihalophenol. The other is that reported by Stamatoff,[15] who prepared the polymer from the sodium salt of 2,4,6-trihalophenol. We employed Stamatoff's method, because it was reported that the PDCPO prepared by the former method has a highly branched structure.[16] Hirose et al.[13] reported a dielectric study on PDCPO prepared by Stamatoff's method and found that the relaxation time was much shorter than that calculated from the Rouse–Zimm theory. Although they did not provide a reason for this discrepancy, it is highly likely that the discrepancy is due to the presence of branches. The principal objective of the present study is to clarify the dielectric normal mode process of PDCPO in dilute solution, with special interest in the effect of chain branching on the dielectric behavior.

Theory

The polarization p per unit electric field for a polymer molecule having a uniaxially parallel dipole moment in dilute solution was described by Zimm[3] and also by Stockmayer and Baur[4] more generally in terms of the "bead-and-spring model".[17] When the number of beads, mean distance between neighboring beads, and dipole moment per unit chain length are N, b, and μ, respectively, p for the polymer in a solvent with a dielectric constant ϵ_s may be written as[4]

$$p = \frac{8N\mu^2b^2(\epsilon_s + 2)^2}{27\pi^2k_BT} \sum_{k\ \mathrm{odd}} k^{-2}(1 + i\omega\tau_k')^{-1} \tag{1}$$

where k and τ_k' denote, respectively, the number of normal modes and the relaxation time for the kth mode. k_BT has the usual meaning. Note that the mode for $k = 1$ contributes dominantly to the polarization (81% of the total polarization). According to Zimm, τ_k' is equal to $2\tau_k$, and for the free-draining case,[5] τ_k is given by

$$\tau_k = 6M\eta_s[\eta]/(\pi^2RTk^2) \tag{2}$$

where M, η_s, and $[\eta]$ denote molecular weight, solvent viscosity, and intrinsic viscosity, respectively. For the non-free-draining case, τ_k is given by[3]

$$\tau_k = M\eta_s[\eta]/(0.586RT\lambda_k') \tag{3}$$

where λ_k' is an eigenvalue calculated by Zimm et al.[18] By use of the relation $\sum_{\mathrm{odd}}k^{-2} = \pi^2/8$, the magnitude of the dielectric dispersion derived from eq 1 is written

$$\frac{\epsilon_0 - \epsilon_\infty}{C} = \frac{4\pi N_A\mu^2\langle r^2\rangle(\epsilon_s + 2)^2}{27k_BTM} \tag{4}$$

where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constant and C, N_A, and $\langle r^2\rangle$ denote, respectively, the concentration in polymer weight per unit volume, Avogadro's number, and the mean square end-to-end distance. We note that $(\epsilon_0 - \epsilon_\infty)/C$ is proportional to $\langle r^2\rangle/M$ and hence is independent of molecular weight in the Θ state.

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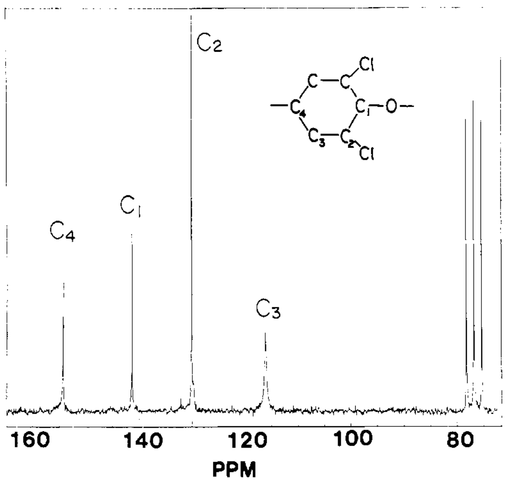


Figure 1. ^{13}C NMR spectrum for the PDCPO (P2) solution in $CDCl_3$. The resonance lines are assigned to C_1, C_2, C_3, and C_4 as shown in the figure based on the calculated chemical shifts.[24] The lines around 80 ppm are due to solvent.

Table I
Characterization of the Samples

code	$10^{-5}M_w$	$[\eta]$, cm^3 g^{-1}	M_w/M_n	$M_w(b)/M_n(b)^a$
P1	6.31	36.8	1.72	8.5
P2	3.80	33.5	1.50	8.0
P3	1.57	24.4	2.57	4.0
P4	0.90	18.2	2.15	2.57
P5	0.45	14.7	1.47	2.20
P6	0.19	10.4	1.22	
P7	13.8	51.4	1.36	9.4
P8	9.33	47.9	1.45	
P9	0.17	9.82	1.26	
P10	0.14	7.28	1.15	
P11	0.068	5.57	1.18	

[a] $M_w(b)/M_n(b)$ denotes the ratio of weight- and number-average molecular weights of the branches calculated with eq 16.

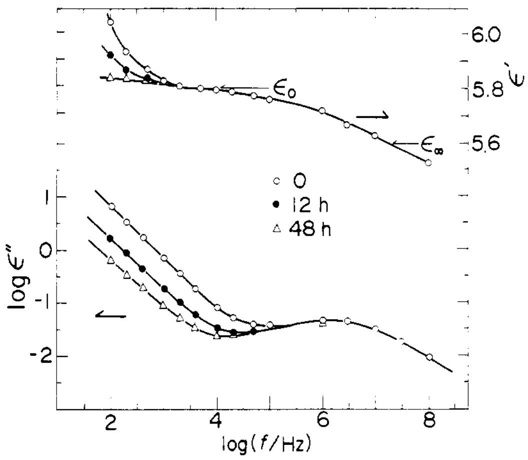


Figure 2. Effect of a static electric field of 100 V cm^{-1} on the frequency dependence of ϵ' and log ϵ'' at 300 K for the P2 solution in chlorobenzene. The period of the application of the dc field is given in this figure.

Experimental Section

1. Material. The samples of PDCPO were prepared from sodium 4-bromo-2,6-dichlorophenol by Stamatoff's method,[15] following the procedure described by Hay.[19] It was found that a trace amount of water in the reaction system affected strongly the yield and molecular weight of the product. Therefore, the monomer was dried at 90 °C under a vacuum of 10^{-1} Pa for 15 h. The solvents used for this synthesis were also dried with CaH_2. We found that the average molecular weight of the product increased with increasing amount of initiator (benzoyl peroxide). We utilized this tendency to control the molecular weight. The mechanism of the polymerization of sodium 2,4,6-tribromophenol was discussed by Hirose et al.[20] They suggested a mechanism similar to that proposed by Staffin and Price for the polymerization of 2,6-dimethyl-4-bromophenol by oxidative displacement of halogen.[21] Since initiation of the polymerization involves formation of benzoyl peroxide radical, Hirose et al. proposed a mechanism very similar to free radical addition polymerization, though the resultant reaction propagates by a condensation mechanism. The dependence of molecular weight on the amount of initiator may be explained by a quinone–ketal redistribution mechanism.[19,20] The probability of the occurrence of this reaction will increase with increasing number of radicals and therefore molecular weight increases with amount of benzoyl peroxide.

The reaction products were fractionated with chloroform/methanol mixed solvents, and PDCPO samples with narrow molecular weight distributions were prepared. The weight- and number-average molecular weight, M_w and M_n, respectively, were determined by gel permeation chromatography (GPC) by using an instrument (Toyo Soda HLC-801A) equipped with a low-angle light scattering detector. The method of M_w and M_n determination by GPC has been reported previously.[23,24] Intrinsic viscosity was determined at 300 K in chlorobenzene with a capillary viscometer. Results of characterization for the PDCPO samples are given in Table I.

Since the polymerization of sodium 4-bromo-2,6-dichlorophenol proceeds by a condensation mechanism with elimination of NaBr, it seems likely that there is a small probability of elimination of the Cl atom at the ortho position. When this occurs, the monomer unit is incorporated into the polymer molecule by a bond at the ortho position. The content of monomer units having ortho linkages was determined to be 2 ± 1% by chemical analysis. We attempted to determine the content of branches by ^{13}C NMR at 90 MHz (JEOL FX90 spectrometer). A representative NMR spectrum is shown in Figure 1. The characteristic resonance lines due to branching[24] were expected to occur around 100 and 110 ppm but they were not observed in the spectrum of our samples at the S/N ratio of about 100. For PDCPO prepared from the copper complex of trihalophenol, Harrod et al.[24] reported more complex NMR spectra. Our spectrum has a simpler pattern than those reported by them, indicating our PDCPO samples contain less irregularities than the samples used by them.

2. Measurements. Dielectric measurements were carried out with transformer-type bridges (General Radio 1615-A and Showa Denki) in the frequency range from 100 Hz to 1 MHz and with a Twin-T type bridge (Fujisoku DLB 1101D) in the range from 1 to 100 MHz. All measurements were made on chlorobenzene solutions at 300 K and at concentrations of 2.5% by weight or less.

Results

The frequency dependence of the dielectric constant ϵ' and the logarithm of the dielectric loss factor ϵ'' for a 2.5% (by weight) solution of P2 are shown in Figure 2. Two dielectric dispersions are visible at about 100 Hz and 1 MHz. Similar behavior was observed in all other samples. Although the change in ϵ' is seen around 100 Hz, a maximum in ϵ'' cannot be seen in the same frequency region. There are two features that indicate this dispersion can be ascribed to an interfacial polarization due to a small amount of impurity ions; i.e., the slope of the log ϵ'' vs. log f curve around 100 Hz was close to −1 and as shown in Figure 2, both ϵ' and log ϵ'' decreased by application of a static electric field of about 100 V cm^{-1}. The latter feature indicates that impurity ions move toward the electrodes under a static electric field and eventually discharge at the electrodes. Thus the dispersion around 100 Hz can be assigned to a dispersion due to impurity ions. On the other hand, the dispersion around 1 MHz was not influenced by a static field and can be assigned to the normal mode process, as discussed later.

Figure 3 shows a representative frequency dependence curve of ϵ' and ϵ''. As seen in this figure, the frequency of maximum loss f_m shifts to lower frequency with in-

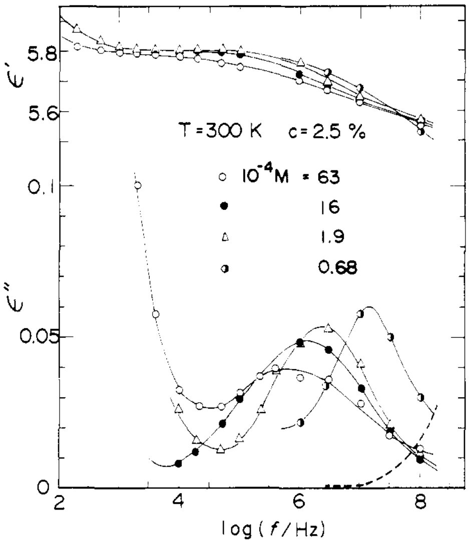


Figure 3. Frequency dependence of ϵ' and ϵ'' at 300 K for solutions of P1 (○), P3 (●), P6 (△), and P11 (◑). The concentrations of these solutions are given in Table II. The chain line represents ϵ'' for the pure solvent.

creasing molecular weight. We can also recognize that the half-width of the loss curve increases with increasing molecular weight.

In Figure 3, the contribution of the solvent to ϵ'' was subtracted from ϵ'' for the solutions, and the values of ϵ''(soln) − ϵ''(solvent) are plotted in the range above 1 MHz. However, we plotted ϵ' without subtraction of the contribution from the solvent. As seen in Figure 3, the value of ϵ' is almost independent of frequency in the range from 1 to 10 kHz. Therefore the value of ϵ' at about 3 kHz may be regarded as the static (relaxed) dielectric constant ϵ_0 for the normal mode process. On the other hand, the high-frequency (unrelaxed) dielectric constant for solutions, ϵ_∞(soln), may be estimated by

$$\epsilon_\infty(\mathrm{soln}) = V_{\mathrm{solv}}\epsilon_{\mathrm{s}} + V_{\mathrm{polym}}n^2 \tag{5}$$

where V_{solv} and V_{polym} denote volume fractions of the solvent and the polymer, respectively, ϵ_{s} (=5.60 at 300 K and at 100 MHz) is the dielectric constant of the solvent, and n is the refractive index of the polymer. It is noted that ϵ_∞(soln) is slightly different from ϵ_∞ defined by eq 4 because ϵ_∞(soln) includes the relaxation in solvent. Assuming that V is equal to the weight fraction of each component and that the value of n^2 is equal to the dielectric constant of bulk (glassy) PDCPO ($n^2 = 3.29$ at 300 K),[25] we have estimated ϵ_∞(soln) to be 5.54. This is a reasonable value compared with the dielectric constant of the solutions at the highest frequency (100 MHz).

The magnitude of the dielectric dispersion $\epsilon_0 - \epsilon_\infty$ was calculated from the area under the loss peak of ϵ'' vs. log f curves on the basis of the relation

$$\epsilon_0 - \epsilon_\infty = (2/\pi)\int \epsilon''\,\mathrm{d}\ln f \tag{6}$$

Since the loss due to ionic conduction ϵ''(ion) and the loss due to the normal mode process overlap, it is necessary to subtract the contribution of ϵ''(ion) from the observed ϵ'' for the calculation of eq 6. In order to estimate ϵ''(ion), Jones et al.[11] determined the ionic conductivity in their sample solutions by extrapolation of $f\epsilon''$ against f^2 to zero frequency. For our samples, we also estimated the ionic conductivity by means of this method. However, it was found that the ionic conductivity thus determined is nearly equal to the conductivity g at 100 Hz. This is not surprising because the frequency of 100 Hz is far away from the relaxation region. Therefore we assumed that ϵ'' at 100 Hz is totally due to ionic conduction and determined the ionic conductivity g by using the relation

$$\epsilon''(\mathrm{ion}) = g/(\omega C_0) \tag{7}$$

where ω and C_0 denote angular frequency and the capacitance of the empty capacitance cell, respectively. Since g should be independent of frequency, we can determine ϵ''(ion) in terms of eq 7. The values of $\epsilon_0 - \epsilon_\infty$ thus calculated are listed in Table II together with the width Δ of the loss peak. For a solution of P2, ϵ_0 and ϵ_∞ are shown in Figure 2.

Table II
Concentration C, Magnitude of Dispersion $\epsilon_0 - \epsilon_\infty$, and Half-Width of Loss Peak Δ

code	10^2C, g cm^{-3}	$\epsilon_0 - \epsilon_\infty$	$(\epsilon_0 - \epsilon_\infty)/C$, cm^3 g^{-1}	Δ
P1	2.70	0.173	6.4	2.85
P2	2.75	0.183	6.7	2.82
P3	2.75	0.185	6.7	2.46
P4	2.63	0.163	6.2	2.20
P5	2.76	0.169	6.1	2.10
P7	2.75	0.193	7.0	2.90
P9	2.75	0.184	6.7	1.72
P10	2.76	0.171	6.2	1.60
P11	2.75	0.167	6.1	1.60

Discussion

1. Relaxation Mechanism. For polymers with repeat units having dipole moments perpendicular to the chain direction, many authors have confirmed that the dielectric relaxation time is independent of molecular weight.[26,27] In contrast to these polymers, the dielectric relaxation time for PDCPO increases with increasing molecular weight as shown in Figure 3. If the PDCPO molecule is a rodlike polymer, it will exhibit a molecular weight dependent relaxation time. However, the molecular weight dependence of the intrinsic viscosity indicates that the conformation of this molecule is a random coil. Therefore the dielectric relaxation in the PDCPO solution may be assigned to the normal mode process. However, we have to take into consideration that the relaxation time for overall rotation[1,28] of a random coil is also represented by an equation similar to eq 2. Stockmayer and Matsuo[29] showed that some halogenated polystyrenes, which have a perpendicular dipole, exhibit a molecular weight dependent relaxation time in the range $M < 10^4$. They ascribed this behavior to overall rotation of the polymer molecule which is faster than the segmental motion at such a low value of M. Since it is difficult to distinguish the normal mode process from overall rotation, we can regard the observed dielectric relaxation process as a combination of both processes.[1] The analysis of the dielectric data can be made based on eq 2 and 3 by neglecting a slight difference in the front factor between the two processes.

2. Analysis of Dipole Moment. As mentioned above, the PDCPO samples seem to contain irregularities in the molecule. Since these "defects" have dipoles oriented perpendicular to the chain contour, they will cause an additional dielectric dispersion due to segmental motion. In this section, the parallel and perpendicular components of the dipole moment are discussed for the sake of the detailed analysis of the dielectric data.

The bond moments that contribute to the dipole moment of the repeat unit are from the C–Cl, C–O, and C–H bonds. Since the repeat unit has a structure symmetric with respect to the O–C_1–C_4 axis (see Figure 1), there is no component of dipole moment in the direction perpendicular to the O–C_1–C_4 axis. Since the C–Cl and C–O

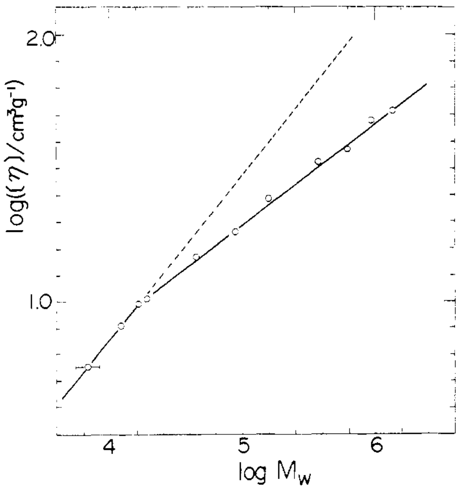


Figure 4. M_w dependence of the intrinsic viscosity $[\eta]$ at 300 K in chlorobenzene.

bonds are at an angle of 60°, the sum of the two dipole vectors for the C–Cl bonds is equivalent to a single C–Cl dipole placed on the O–C_1–C_4 axis. The same argument can be applied to the C–H bonds. On the other hand, the contribution of the C–O bonds may be negliglble because the vectors of the C_1–O and C_4–O bonds cancel each other. Therefore the dipole moment of the repeat unit is approximately equal to that of chlorobenzene,[30] 1.56 D. From the data on bond lengths,[31] the length of the repeat unit O–O distance is calculated to be 0.550 nm. Thus the value of μ in eq 1 becomes 2.85×10^{-11} cgs esu.

Two possible origins for the occurrence of perpendicular dipoles may be considered. They are monomers linked at the ortho position and the head-to-head linkage. From the structure of the ortho-linked repeat unit, the effective perpendicular dipole moment for this unit is estimated to be about 1.6 D because the dipole moment of the C–Br bond[25] is 1.57 D. The content of the ortho-linked units is less than 3% as described in the Experimental Section. From these values, the contribution of this process to ϵ'' was calculated to be less than 4×10^{-4} for the solution with 2.5% concentration. We note that the contribution of the ortho-linked unit is 2 orders smaller than the observed value of ϵ''. If the head-to-head linkage occurs, a peroxide bond (C–O–O–C) will be formed. However, the infrared spectrum of the PDCPO film exhibited no bands characteristic of –O–O– bonds around 1800 cm^{-1}. It is also pointed out that the peroxide bond is unstable and is decomposed soon if it exists. Therefore the possibility of the occurrence of the head-to-head linkage can be ruled out. Accordingly, we can conclude that the contribution of the perpendicular dipole is negligibly small.

3. Degree of Branching. As described above, there exists a possibility that the PDCPO molecule contains branches. We examine the degree of branching by analyzing the intrinsic viscosity, $[\eta]$. Figure 4 shows the molecular weight dependence of $[\eta]$. As can be seen in Figure 4, the slope of the log $[\eta]$ vs. log M_w curve changes at $M_w = 1.75 \times 10^4$. The constant α in the Mark–Houwink–Sakurada equation, $[\eta] = KM^{\alpha}$, is 0.62 in the range $M_w < 1.75 \times 10^4$ and is a typical value for flexible polymers in a good solvent, while in the range $M_w > 1.75 \times 10^4$, α is 0.38, smaller than in a Θ solvent. This indicates that there is a definite probability of branching in the process of polymerization. When the degree of polymerization is small, the PDCPO molecule is linear, but with the growth of the chain, branches may appear as shown schematically in Figure 5. From eq 4 the intrinsic viscosities of linear and branched PDCPO, referred to as $[\eta]_l$ and $[\eta]_b$, respectively, are given by

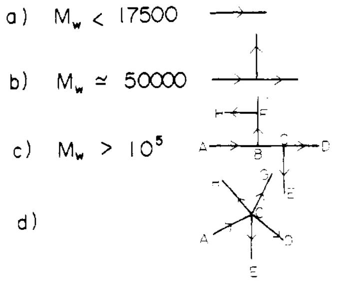


Figure 5. Schematic illustration of the linear and branched PDCPO molecules. Arrow indicates the direction of dipoles.

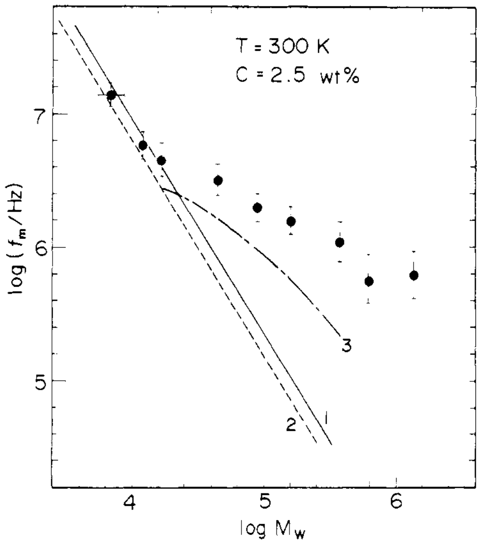


Figure 6. Molecular weight (M_w) dependence of the frequency of the loss maximum f_m measured at 300 K for solutions of 2.5% concentration. Curves 1–3 represent the theoretical relaxation frequencies for the various conditions: curve 1, linear molecule, nondraining; curve 2, linear molecule, free draining; curve 3, star polymer, free draining.

$$\log [\eta]_l = 0.62 \log M_w - 1.63 \tag{8}$$

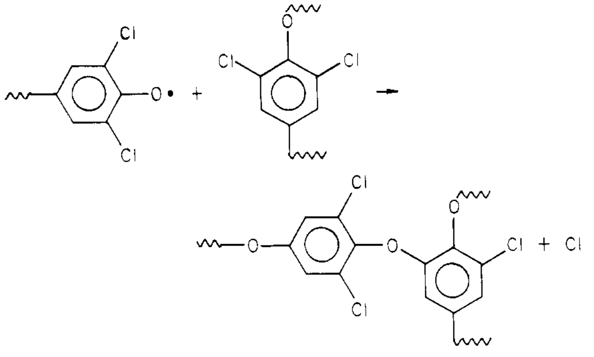
$$\log [\eta]_b = 0.38 \log M_w - 0.615 \tag{9}$$

Assuming that the branched PDCPO is a star-shaped polymer having j arms of equal length, we have estimated the number of branches (j) from the ratio $[\eta]_l/[\eta]_b$ based on the theories for the case of free draining[32] and for the case of nondraining.[33] For example, the value of j for the PDCPO with molecular weight of 10^5 is determined to be 4 and 6, respectively, in the case of free draining and nondraining. This implies that there exists one branch per 2×10^4 molecular weight on the average. We note that this number of branches is too small to be detected with our ^{13}C NMR spectrometer.

4. Molecular Weight Dependence of the Relaxation Time. The molecular weight dependence of the frequency of the maximum loss f_m for the solutions with 2.5 wt % concentration is shown in Figure 6, in which f_m is compared with the relaxation frequency for the first mode $(2\pi\tau_1')^{-1}$ given by eq 2 and 3. Line 1 in Figure 6 represents the theoretical relaxation frequency in the case of nondraining while line 2 is for the case of free draining. As shown in Figure 6 the observed f_m agrees fairly well with the theoretical f_m in the range of molecular weight less than 2×10^4 while in the range $M > 2 \times 10^4$, the experimental f_m is higher than the theoretical f_m. We note that the molecular weight at which the M dependence of f_m changes agrees well with M at which the M dependence of $[\eta]$ changes. This implies that since the PDCPO molecule with high molecular weight contains branches, the wavelength and hence the relaxation times for the normal modes are shorter than those in the linear molecule with the same molecular weight.

In order to discuss the dielectric relaxation time in the branched PDCPO molecules, it is necessary to specify the dipole direction of the branches. Following is our speculation for this problem.

Since polymeric radicals are formed in the polymerization of sodium trihalophenol, it may be expected that the branches are formed in a manner represented by eq 10;



(10)

i.e., a polymeric radical attacks a chlorine atom of another chain. On the basis of this speculation, we assume that the dipole moments of the branches are always directed from branch points to the end of the branches as shown in Figure 5c.

Again we assume that branched PDCPO molecules are j-star polymers having equivalent arms. For example, the molecule shown in Figure 5c is approximately equivalent to the star polymer shown in Figure 5d. In this figure we note that only the dipole of AO is directed opposite to the other branches and therefore the dielectric relaxation time for the motion including AO and one of the other branches is equal to the longest relaxation time τ_{1j} in a j-star polymer.[32] But for the other branches, the relaxation time corresponds to the second normal mode τ_{2j}'. Generally, we can say that in the model j-star PDCPO, two arms (original main chain) exhibit a relaxation time equal to τ_{1j}' while the other $(j - 2)$ arms exhibit a relaxation time equal to τ_{2j}'. Stockmayer and Burke[10] studied the dielectric relaxation of a 3-star poly(propylene oxide) in which all branches have the same dipole direction. They explained the low-frequency relaxation time with τ_{2j}'. In the present case, the average relaxation time may be given by

$$\tau_j' = [2\tau_{1j}' + (j - 2)\tau_{2j}']/j \qquad (11)$$

Thus the average relaxation time τ_j' for the free-draining case may be equal to $(j + 6)\tau_{12}'/j^3$. Here, τ_{12}' denotes the longest relaxation time of the linear PDCPO molecule having the same molecular weight as a j-star polymer. In the nondraining case, the average relaxation time cannot be written with a simple equation.

By using the value of j estimated from $[\eta]_b/[\eta]_l$, we have calculated the average relaxation frequency for the free-draining case (curve 3 in Figure 6). The result of the calculation agrees roughly with experiment.

5. Distribution of Dielectric Relaxation Time. So far, we calculated the average relaxation time for the branched polymer, assuming a star-shaped polymer with equal arm lengths. Since branching occurs statistically, there exists a distribution of the branch molecular weight, M(b). This is obviously reflected by the half-width Δ of the loss curve listed in Table II. In this section, a relationship between Δ and the ratio M_w/M_n, which is a measure of the distribution of the molecular weight, is discussed.

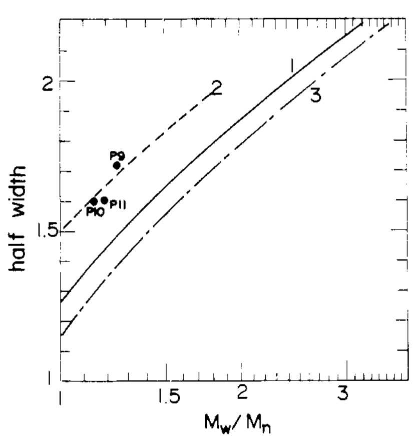


Figure 7. Dependence of the half-width of loss peak on M_w/M_n. Curves 1–3 represent eq 13 with various values of ξ: curve 1, $\xi = 0.574$ (Rouse–Zimm); curve 2, $\xi = 0.482$; curve 3, $\xi = 0.632$ (Debye).

First, we define the average relaxation time τ for a linear PDCPO molecule with molecular weight M by

$$\tau = \sum(\tau_k'/k^2)/\sum(1/k^2) \qquad k \text{ odd} \qquad (12)$$

It is noted that τ is proportional to $M^{1+\alpha}$. We assume that the distribution of molecular weight is given by a logarithmic normal distribution written as

$$w(\ln M) = (c/\pi) \exp[-c^2(\ln M - \ln M_0)^2] \qquad (13)$$

where c and M_0 are constants. With the aid of the linear relation between τ and $M^{1+\alpha}$, eq 13 can be transformed into the distribution function of relaxation time ϕ (ln τ) written as

$$\phi\,(\ln \tau) = [2\pi \ln (M_w/M_n)]^{-0.5} \exp\left[-\frac{(\ln \tau - \ln \tau_0)^2}{2(1 + \alpha)^2 \ln (M_w/M_n)}\right] \qquad (14)$$

where τ_0 is a constant and relation given by $M_w/M_n = \exp(1/2c^2)$ has been used. The frequency dependence of the dielectric loss is generally written in the form

$$\epsilon'' = \int \phi\,(\ln \tau) D(f,\tau)\, \mathrm{d} \ln \tau \qquad (15)$$

where $D(f,\tau)$ denotes the frequency dependence of ϵ'' for a molecule with relaxation time τ. Since this integral cannot be written by elementary functions, $D(f,\tau)$ is replaced with a Gaussian function given by $(1/2) \exp[-\xi^2(\ln (2\pi f\tau))^2]$. The parameter ξ should be determined so that the half-width of this function is equal to that of $D(f,\tau)$ and is equal to 0.574 for a normal mode process. In this way the width Δ on a $\log_{10} f$ scale is written as

$$\Delta = (0.72314/\xi)[1 + 2\xi^2\,(1 + \alpha)^2 \ln (M_w/M_n)]^{0.5} \qquad (16)$$

This relation is depicted in Figure 7 by using $\alpha = 0.62$ and is compared with the observed width for the linear PDCPO.

As seen in Figure 7, the experimental Δ is slightly broader than the theoretical Δ. This discrepancy is considered to arise from the Gaussian approximation and also from a nonexponential time correlation function for the each normal mode. The latter reason is adduced because for many cases, the autocorrelation function for the motion of dipoles is not exponential and therefore the width of the loss curve is broader than the width given by the Debye equation.[34,35] Due to these reasons we regard ξ as an adjustable parameter. As shown by the chain line in Figure 7, the best-fit curve has been obtained by taking $\xi = 0.482$.

From the value of Δ for the branched PDCPO, the distribution of the chain lengths of branches, including the main chain, can be assessed in terms of eq 16. In this calculation, ξ and α are taken to be 0.482 and 0.62, respectively. The values of $M_w\,(b)/M_n\,(b)$ thus calculated are listed in Table I. As expected, $M_w\,(b)/M_n\,(b)$ is much larger than M_w/M_n for the whole molecule and increases with molecular weight.

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Registry No. Poly[oxy(2,6-dichloro-*p*-phenylene)], 26023-26-7; 2,6-dichlorophenol homopolymer, 25511-62-0.

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Notes

Concentration Dependence of the Translational Diffusion Coefficient of Unperturbed Flexible Chains

YOSHISUKE TSUNASHIMA* and NORIO NEMOTO

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan. Received March 24, 1983

The dynamic light scattering (DLS) technique provides direct and highly accurate measurements of the concentration dependence of the diffusion coefficient of a polymer in solution in comparison with other techniques such as sedimentation diffusion (ultracentrifuge, SD) or conventional diffusion over a wide range of polymer molecular weight M. With the results, the theories on the coefficient k_D for flexible chains in dilute solutions can be discussed in detail for the polymer models used and the treatment of the hydrodynamic interactions. In this note, we sum up the experimental results of k_D for linear, narrow-molecular-weight polystyrenes (PS) at the Θ temperature, including our recent data,[1] and point out a weaker molecular weight dependence of k_D^Θ than expected from the theoretical expressions ($k_D^\Theta \propto M^{1/2}$) of Pyun and Fixman,[2] Yamakawa[3] and Imai,[4] or the recent report of Mulderije.[5]

We may expand the diffusion coefficient D for monodisperse linear polymers as a function of concentration c (g cm^{-3})

$$D = D_0(1 + k_D^\Theta c + ...) \tag{1}$$

where D_0 is the translational diffusion coefficient at infinite dilution and proportional to $M^{1/2}$. The theoretical predictions available at present for k_D^Θ may be expressed as

$$k_D^\Theta = -(k_f^\Theta + \bar{v}) \tag{2}$$

with

$$k_f^\Theta = BN_A v_H/M = B'M^{1/2} \tag{3}$$

where $\bar{v}$ is the partial specific volume of the polymer, k_f^Θ the coefficient of the concentration dependence of the friction coefficient, N_A the Avogadro number, and v_H the hydrodynamic volume of the polymer at infinite dilution. The Einstein–Stokes law expression for D_0

$$D_0 = k_BT/6\pi\eta_0R_H \tag{4}$$

and the relation at infinite dilution $v_H = (4\pi/3)R_H^3$ lead to the second equality in eq 3. Here, η_0 is the solvent viscosity and R_H the hydrodynamic radius of the polymer. Thus all the theories available require an $M^{1/2}$ dependence of k_D^Θ in the larger M region because $\bar{v} \simeq 1$ (cm^3 g^{-1}). The difference in these theories is revealed only in the magnitude of the constant value B in eq 3. The Yamakawa[3a]–Imai[4] (Y–I) theories for bead–spring model chains lead to $B = 1$, while the Pyun–Fixman (P–F) soft-equivalent-sphere model gives $B = 2.23$. Mulderije[5] has recently revised the P–F value as $B = 2.06$, moreover indicating $B = 1.60$, which is based on the study of the hard spherical particles.[6]

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